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(54) Title: MACHINE DISHWASHING COMPOSITIONS			
(57) Abstract			
A co-granule of a hydrotalcite like material, preferably a Zn/Al or Mg/Al hydrotalcite, and an alkali metal silicate constitutes a good alternative to synthetic hectorites normally used in machine dishwashing compositions.			
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MACHINE DISHWASHING COMPOSITIONSFIELD OF THE INVENTION

5 This invention relates to machine dish- and warewashing compositions. These compositions are used for the cleaning of housewares in automatic-dishwashing and warewashing machines and will be referred to in the description as
10 machine dishwashing compositions.

The invention more specifically relates to a substitute to synthetic hectorites for use in machine dishwashing compositions.

BACKGROUND OF THE INVENTION

Machine dishwashing compositions usually contain as main components a builder or builder mixture, buffering and/or
20 alkaline agents, a bleaching agent which may be a chlorine or oxygen bleach, and lately also enzymes. Such machine dishwashing compositions are used in the main wash step of machine dishwashing and in general have a satisfactory cleaning performance.

25 It is, however, well known in the dishwashing art that the visual appearance of the cleaned article is a critical factor for a dishwashing composition to be satisfactory to the consumer. Frequently after cleaning of an article a
30 film is formed thereon, which results in the article showing a dull surface when dry, or spots are formed on an article upon drying, both phenomena causing the article to have an "unclean" visual appearance.

It is customary to add to the rinsing water a rinse aid composition which causes the articles to dry more evenly and improves the visual appearance of the articles when dry. Although such rinse aid compositions improve said visual appearance in comparison with articles which have not been rinsed with a rinse aid containing rinse liquor, said visual appearance may still need improvement, as, despite the use of a rinse aid, some film- and spot-formation may still occur.

It is known from EP-A-0,139,329, EP-A-0,139,331 and EP-A-0,140,435 that the incorporation of an effective level of a layered clay in machine dishwashing compositions reduces the problem of film and spot formation on the washed articles, thereby improving the so-called "glass appearance". EP-A-0139.330 discloses the incorporation of a layered clay in a rinse aid composition.

Suitable layered clay minerals according to these art references belong to the geological classes of the smectites, the kaolins, the illites, the chlorites, the attapulgites and the mixed layer clays, which may be either naturally occurring or synthetic, preferably the commercial synthetic hectorites ex Laporte Industries Ltd, known under the tradename Laponite®.

Although the glass appearance benefit of Laponite® clay can indeed be demonstrated synthetic hectorites are expensive products.

There is therefore a need for a substitute to synthetic hectorites which, on the one hand will be at least as effective and, on the other hand will constitute an economically interesting alternative.

It is a first goal of the invention to provide a substitute to synthetic hectorites for use in machine dishwashing compositions.

5 It is a second goal of the present invention to provide a machine dishwashing composition containing said synthetic hectorites substitute.

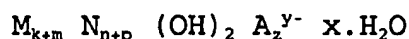
Definitions

10

i) Hydrotalcite-like Material

By hydrotalcite-like material, it is understood a product having the following composition:

15



where:

20

M is any 1+ or 2+ cation or combination thereof

N is any 3+ or 4+ cation or combination thereof

k is the sum of the individual mole fractions of the 1+ cations

m is the sum of the individual mole fractions of the 2+ cations

25

n is the sum of the individual mole fractions of the 3+ cations

p is the sum of the individual mole fractions of the 4+ cations

30

where either but not both of k and m or n and p can be zero and $k+m+n+p=1$.

A_z^{y-} is any anion of charge y^- and mole fraction z , or combination of anions of similar or differing y^- and $k+2m+3n+4p-2-zy=0$ and x can range from 1 to 100.

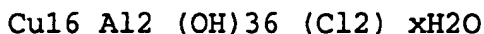
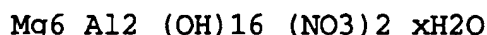
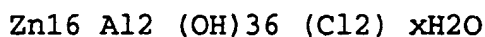
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Examples of the cations M in the above formula are Li, Mg^{2+} , Zn^{2+} , Fe^{2+} , Cu^{2+} , Sn^{2+} , Ca^{2+} and Sr^{2+} . Suitable N cations include Al^{3+} , Fe^{3+} , Ti^{4+} and Sn^{4+} .

5 Preferred divalent cations are Zn^{2+} , Cu^{2+} or Mg^{2+} or a combination of these ions, or a combination with other divalent cations.

10 The anion A may be an inorganic or organic anion. Preferred inorganic anions A are Cl^- , NO_3^- , SO_4^{2-} , CO_3^{2-} and OH^- . Examples of organic anions are carboxylate ions such as citrate and stearate.

15 Examples of hydrotalcite-like materials of this invention are:-



20 Preparation of hydrotalcite-like compounds is known and has been described in a number of publications including Solid State Ionics 22 (1986) pages 135-141 where there is published a paper by Walter T Reichle entitled "Synthesis of Anionic Clay Minerals (Mixed
25 Metal Hydroxides, Hydrotalcite)" and Chemtech (January 1986) pages 58-63 where there is published a paper by Walter T Reichle entitled "Anionic Clay Minerals".

30 ii) The Builder Material

Builder materials (phosphates and non-phosphate builder materials) are well-known in the art and many types of organic and inorganic compounds have been described in literature. They are normally used in all sorts of
35 cleaning compositions to provide alkalinity and

buffering capacity, prevent flocculation, maintain ionic strength, extract metals from soils and/or remove alkaline-earth metal ions from washing solutions.

5 The builder material usable herein can be any one or mixture of the various phosphate and preferably non-phosphate builder materials, such as for example the alkalimetal citrates, carbonates and bicarbonates; nitrilotriacetic acid (NTA); dipicolinic acid (DPA);
10 oxydisuccinic acid (ODS); alkyl- and alkenylsuccinates (AKS); layered silicate; and zeolites. They may be present in the composition of the invention in an amount of from 10% up to about 90% by weight, preferably from 20% to 80% by weight. Particularly
15 preferred builders are citrates, alkenylsuccinates, carbonates, bicarbonates, zeolites, and mixtures thereof.

iii) The Buffering and/or Alkaline Agent

20 This is normally an alkalimetal silicate, preferably sodium silicate at a level of from about 1 to about 70% by weight, preferably from 5 to 40% by weight. This material is employed as a cleaning ingredient, source
25 of alkalinity, metal corrosion inhibitor and protector of glaze on china tableware. Typically, silicates with a mol ratio of SiO_2 :metal oxide of 0.67 to 4.5 are suitable. Especially effective is sodium silicate having a mol ratio of SiO_2 : Na_2O of from about 1.0 to
30 about 3.3., preferably from about 1.8 to about 2.5, normally referred to as sodium disilicate.

NaOH and/or KOH are also commonly used to provide alkalinity in compositions for industrial warewashing
35 machines.

iv) The Bleaching Agent

If present the amount of bleaching agent will preferably lie in a range from 1 to 30% by weight.

5 Alkali metal hypochlorite may be incorporated. Other chlorine bleaches are alkali metal salts of di- and tri-chloro and di- and tri-bromo cyanuric acids.

10 Preferred bleaches are the peroxygen bleaches, such as sodium perborate (tetra- or monohydrate) or sodium percarbonate. These are preferably used in conjunction with a bleach activator which allows the liberation of active oxygen species at a lower temperature. Numerous examples of activators of this type, often also
15 referred to as bleach or peracid precursors, are known in the art. Preferred bleach activators are tetraacetyl ethylene diamine (TAED), glucose pentaacetate (GPA) and the mono-long chain acyl tetraacetyl glucoses as disclosed in WO 91/10719, but
20 other activators such as choline sulphophenylcarbonate (CSPC) as disclosed in US Patents 4,751,015 and 4,818,426 can be used. The amounts of sodium perborate or percarbonate and bleach activator in the compositions preferably do not exceed 20% and 10% by
25 weight respectively, e.g. from 4-20% and from 2-10% by weight respectively.

Another peroxygen bleach is potassium monopersulphate. Further peroxygen bleaches which may be used are the
30 organic peroxyacids and their metal salts. Typical peroxy-acids include:

- i) peroxybenzoic acid and ring-substituted peroxybenzoic acids, e.g. peroxy- α -naphthoic acid;
- 35 ii) aliphatic and substituted aliphatic monoperoxy

acids, e.g. peroxyauric acid and peroxyauric acid;

iii) 1, 12-diperoxydodecanedioic acid (DPDA);

iv) 1, 9-diperoxyazelaic acid;

5 v) diperoxybrassylic acid; diperoxysebacic acid and diperoxyisophthalic acid;

vi) 2-decyldiperoxybutane-1,4-dioic acid; and

vii) phthaloylamido peroxyacaproic acid (PAP)

10 Instead of or together with said bleach activators, a bleach catalyst, such as the manganese complexes of EP-A-458,397 and the sulphonimines of US Patents 5,041,232 and 5,047,163 may also be added.

15 v) Enzymes

Amylolytic and/or proteolytic enzymes are normally used. The amylolytic enzymes usable herein can be those derived from bacteria or fungi. Preferred
20 amylolytic enzymes are those prepared and described in GB Patent No. 1,296,839, cultivated from the strains of *Bacillus licheniformis* NCIB 8061, NCIB 8059, ATCC 6334, ATCC 6598, ATCC 11945, ATCC 8480 and ATCC 9945 A.

25 Examples of such amylolytic enzymes are those produced and distributed under the Trade-names of SP-95[®] and Termamyl[®] by Novo Industri A/S, Copenhagen, Denmark. These amylolytic enzymes are generally presented as granules and may have enzyme activities of from about 2 to 10 Maltose units/milligram. They may be present in
30 the composition of the invention in amounts such that the final composition has amylolytic enzyme activity of from 10³ to 10⁶ Maltose Units/Kilogram.

35 The amylolytic activity as referred to herein can be determined by the method as described by P. Bernfeld

in "Method of Enzymology" Volume I (1955) page 149.

5 The proteolytic enzymes usable herein are for example
the subtilisins which are obtained from particular
strains of B. Subtilis and B. licheniformis, such as
the commercially available subtilisins Maxatase®
supplied by Gist-Brocades NV, Delft, Holland, and
Alcalase®, supplied by NOVO Industri A/S Copenhagen,
Denmark. Particularly suitable are proteases obtained
10 from a strain of Bacillus having maximum activity
throughout the pH range of 8-12, being commercially
available from NOVO Industri A/S under the Trade names
of Esperase® and Savinase®. The preparation of these
and analogues enzymes is described in GB Patent No.
15 1,243,784. These enzymes are generally presented as
granules, e.g. marumes, prills, T-granulates etc., and
may have enzyme activities of from 500 to 1700 Glycine
Units/mg. The proteolytic enzyme activity can be
determined by the method as described by M.L. Anson in
20 "Journal of General Physiology" Vol. 22 (1938), page 79
(one Anson unit/gram = 733 Glycine Units/milligram).

In the compositions of the invention proteolytic
enzymes may be present in amounts such that the final
25 composition has proteolytic enzyme activity of from
about 10^6 to 10^8 Glycine Units/Kilogram.

Other enzymes, such as lipolytic enzymes may also be
incorporated to improve fat removal. Typical examples
30 of commercial lipolytic enzymes are Lipase YL, Amano
CE, Wallerstein AW, Lipase My, and Lipolase ex Novo
Ind.

Testsi) Spot Test

5 The following powdered machine dishwashing composition were prepared:

	<u>Composition</u>	<u>Parts by Weight</u>
10	Sodium citrate 2 aq.	42
	Sodium disilicate ⁴⁾	35
	Sodium perborate monohydrate	8.4
	Sokalan CP5 ³⁾	5
	TAED ²⁾ (83%)	5
15	Amylase	1.7
	Protease	1.7
	Adsorbing material ³⁾	1.2

20 1) = acrylic acid/maleic acid copolymer ex BASF

2) = N, N, N¹, N¹-tetraacetylene diamine bleach activator

25 3) = a) Laponite XLG ex Laporte Industries Ltd
b) Synthetic hydrotalcite, $[\text{Mg}_6\text{Al}_2(\text{OH})_{16}]\text{CO}_3 \cdot 4\text{H}_2\text{O}$
obtainable from Joseph Crosfield and Sons -
Warrington - U.K. under the tradename
Macrosorb CT100

30

4) Obtainable from Joseph Crosfield and Sons -
Warrington - U.K. under the tradename Pyramid G82.

Machine dishwashing experiments were carried out with the above formulations (a) and (b) at a product dosage of 17 g. per run (= 3.4 g/l) in a Bosch S 510 machine at a water intake of 5 litre (16°FH). The wash programme consisted of a pre-wash, main wash at 55°C, two intermediate rinses and a final rinse of 65°C. Total washing time 65 minutes. The load per wash consisted of a dummy load together with five milk-glasses and two glass-plates. As in glass appearance terms egg yolk is notoriously known as problem-soil, it is used here as the standard-soil. The machine dishwashing product and egg-yolk soiling (a dispersion of 2g egg yolk in ca. 20 ml water) were added to the wash-liquor at the start of the main wash cycle.

The glass-appearance was judged in terms of spot-score according to the following table.

Spot - score	Number of spots
1	none
2	1 - 5
3	6 - 10
4	11 - 20
5	21 - 30
6	31 - 40
7	41 - 50
8	51 - 75
9	76 - 100
10	101 - 150
11	> 150

GENERAL DESCRIPTION OF THE INVENTION

It has now surprisingly been found that the above goals can be achieved by the incorporation in a machine dishwashing composition of an effective level of a co-granule of an hydrotalcite-like material, preferably a Zn/Al or Mg/Al hydrotalcite, and a soluble alkali metal silicate.

It is therefore a first object of the present invention to provide a co-granule of an hydrotalcite like material, preferably a Zn/Al or Mg/Al hydrotalcite, and an alkali metal silicate.

A co-granule of an alkali metal silicate which is soluble under machine dish wash conditions and hydrotalcite like material can be prepared by a process involving mixing the alkali metal silicate, which may be in the solution, powder or granular form and the hydrotalcite like material, which may be introduced as a dry powder or as a slurry in water or alkali metal silicate solution. This mixing takes place either in, or is followed by introduction into, suitable granulation equipment (e.g spray drier, roller compactor, fluid bed drier, marumeriser, pan granulator, extruder, tableting machinery or any other suitable equipment). Water or alkali metal silicate solution may optionally be added to assist the granulation step (or as part of the formulation) and a post-granulation drying step may be needed to produce a free-flowing powder.

It is preferred, though not essential, that there is contact between the hydrotalcite like material and the alkali metal silicate in an aqueous phase at some time during the granulation step.

Preferably the weight ratio of alkali metal silicate to hydrotalcite-like material in the cogranule is within the range 500:1 to 1:50.

5 It is also a second object of the present invention to provide a machine dishwashing composition comprising a builder or builder mixture, buffering and/or alkaline agent, wherein it further comprises an effective amount of a co-
10 granule of an alkali metal silicate and a hydrotalcite-like material.

The effective level of the co-granule of alkali metal silicate and hydrotalcite-like material to be included in the machine dishwashing composition of the invention will be
15 such to give a hydrotalcite-like material content which will range from about 0.01 to 40% by weight, usually from 0.1 to 20% by weight, preferably from 0.5 to 10% and most preferably from 0.5 - 5% by weight.

20 The machine dishwashing composition of the invention will normally also contain a builder or builder mixture, buffering and/or alkaline agents, optionally but preferably also a bleaching agent and an enzyme or mixtures of enzymes.

25 The machine dishwashing compositions of the present invention can be manufactured and presented in any physical form such as a powder, liquid, paste or solid blocks or tablets, and are preferably formulated such that they provide a wash liquor with a pH of between 6 and 13,
30 preferably from 8-11, and more preferably from 9.5-10.5 (measured at a concentration of from 0.1-0.3% by weight in water).

SPECIFIC DESCRIPTION OF THE INVENTION

5 The invention will now be illustrated by way of the following examples (percentages are by weight unless otherwise stated).

EXAMPLE 1 - COMPARATIVE EXAMPLE

10 A first spot test was realised as described herein before wherein the absorbent was Laponite XLG ex Laporte Industries Ltd. Laponite XLG and TAED were added as cogranules to the washing composition.

15 The Spot Score was 6.

EXAMPLE 2

20 A second spot test was realised as described herein before wherein the absorbent was $[\text{Mg}_6\text{Al}_2(\text{OH})_{16}]\text{CO}_3 \cdot 4\text{H}_2\text{O}$ obtainable from Joseph Crosfield & Sons - Warrington - U.K. under the trade name Macrosorb CT100.

25 Disilicate and hydrotalcite material were added as cogranules to the washing composition.

The cogranules were produced as follows.

30 2.5 kg of granular sodium disilicate (Pyramid G82 ex-Crosfield) were mixed with 88.2g Macrosorb CT100 (ex-Crosfield) for 3 min in a Lodige plough shear mixer. 400g of a 10% sodium disilicate solution (diluted Crystal 120 ex-Crosfield), heated to 80°C, were sprayed onto this mixture using a Delevan nozzle sprayer. Mixing continued for 5 min. The granulated product was then dried in a
35 fluidised bed at 80°C until the total water content was

23-24% by weight. The 200-1000 micron fraction was sieved out and used in a dishwashing composition as above described.

5 The Spot Score was 9.

EXAMPLE 3

10 A third spot test was realised as described herein before wherein the absorbent was $[\text{Mg}_6\text{Al}_2(\text{OH})_{16}]\text{CO}_3 \cdot 4\text{H}_2\text{O}$ obtainable from Joseph Crosfield & Sons under the trade name Macrosorb CT100.

15 Disilicate and hydrotalcite material were added as cogranules to the washing composition.

The cogranules were produced as follows:

20 2.5 kg of granular sodium disilicate (as in Example 2) were placed in the Lodige mixer. 88.2 g Macrosorb CT100 were mixed with 400g of a 10% sodium disilicate solution using an ultra turrax system then sprayed onto the granular disilicate. Granulation, drying and sieving were done as in Example 2.

25

The Spot Score was 6.

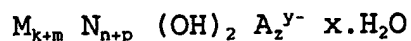
30 Comparing Examples 2 and 3 with Example 1, it can be seen that a cogranule of soluble alkali metal silicate and hydrotalcite-like material constitutes a good alternative to synthetic hectorites.

35 Comparing Example 2 with Example 3, it can be seen that depending on the manufacturing process of the cogranules, the performance of the end-product can be slightly

different. Without wishing to be bound by any theory, it can be assumed that the hydrotalcite like material reacts with the soluble alkali metal silicate in solution to form a complex which could bind proteinaceous species. If this theory is correct, it can be assumed that Example 3 was made via a process which should give controlled and better complexation between the hydrotalcite-like material and the alkali metal silicate.

CLAIMS

1. Cogranule of an hydrotalcite like material and alkali
metal silicate, the hydrotalcite-like material being a
product having the following composition:



where:

M is any 1+ or 2+ cation or combination thereof

N is any 3+ or 4+ cation or combination thereof

k is the sum of the individual mole fractions of
the 1+ cations

m is the sum of the individual mole fractions of
the 2+ cations

n is the sum of the individual mole fractions of
the 3+ cations

p is the sum of the individual mole fractions of
the 4+ cations

where either but not both of k and m or n and p
can be zero and $k+m+n+p=1$.

A_z^{y-} being any anion of charge y^- and mole fraction
z, or combination of anions of similar or
differing y^- and $k+2m+3n+4p-2-zy=0$ and x can range
from 1 to 100.

2. Cogranule according to claim 1 wherein the ratio of
alkali metal silicate to hydrotalcite-like material is
within the range 500:1 to 1:50.
3. Machine dishwashing composition comprising a builder or
builder mixture, buffering and/or alkaline agent,

wherein it further comprises an effective amount of a cogranule of alkali metal silicate and a hydrotalcite-like material according to claim 1 or 2.

INTERNATIONAL SEARCH REPORT

PCT/EP 95, 00102

A. CLASSIFICATION OF SUBJECT MATTER
C 11 D 3/02, C 11 D 17/00

According to International Patent Classification (IPC) or to both national classification and IPC 6

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C 11 D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO, A, 89/08 693 (THE DOW CHEMICAL CO.) 21 September 1989 (21.09.89), page 3, lines 16-34; page 6, line 20 - page 7, line 12; example 5; claims. ---	1-3
X	DE, A, 4 122 200 (HENKEL) 07 January 1993 (07.01.93), the whole document. ---	1-3
P, X	WO, A, 94/03 574 (UNILEVER) 17 February 1994 (17.02.94), page 3, line 18 - page 7, line 29; examples; claims 1-6. ----	1-3

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☐ Patent family members are listed in annex.

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Date of the actual completion of the international search
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Date of mailing of the international search report

03. 05. 95

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PCT/EP 95/00102 SAE 103246

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WD A1 8908693	21-09-89	US A 5015409	14-05-91
		CA A1 1314192	09-03-93
		EP A1 364543	25-04-90
		EP A4 364543	05-09-90
		JP T2 2503688	01-11-90
		JP B4 6062930	17-08-94
		US A 5232627	03-08-93
		AT E 93815	15-09-93
		AU A1 59754/86	22-01-87
		AU B2 595214	29-03-90
		BR A 8603134	24-02-87
		CN A 86104606	04-02-87
		CN B 1016352	22-04-92
		CN A 1063266	05-08-92
		DE C0 3688954	07-10-93
		DE T2 3688954	23-12-93
		DK A0 3203/86	04-07-86
		DK A 3203/86	06-01-87
		EP A2 207811	07-01-87
		EP A3 207811	17-11-88
		EP B1 207811	01-09-93
		ES AF 2000647	16-03-88
		IL A0 79304	31-10-86
		IL A1 79304	12-07-90
		JP A2 62036007	17-02-87
		KR B1 9004487	28-06-90
		NO A0 862726	04-07-86
		NO A 862726	06-01-87
		ZA A 8604992	30-03-88
		US A 4990268	05-02-91
		US A 5154932	13-10-92
		AT E 93213	15-09-93
		AU A1 59756/86	22-01-87
		AU B2 580432	12-01-89
		BR A 8603135	24-02-87
		CA A1 1264926	30-01-90
		CN A 86104614	22-04-87
		CN B 1006801	14-02-90
		DE C0 3688896	23-09-93
		DE T2 3688896	09-12-93
		DK A0 3204/86	04-07-86
		DK A 3204/86	06-01-87
		EP A2 207810	07-01-87
		EP A3 207810	17-11-88
		EP B1 207810	18-08-93
		ES AF 2000457	01-03-88
		IL A0 79303	31-10-86
		IL A1 79303	09-02-90
		IN A 167449	27-10-90
		JP A2 62036481	17-02-87
		JP B4 6099679	07-12-94
		KR B1 9402568	25-03-94
		NO A0 862725	04-07-86
		NO A 862725	06-01-87
		NO B 175598	25-07-94
		NO C 175598	02-11-94
		US A 4664843	12-05-87
		ZA A 8604991	30-03-88
		US A 4790954	13-12-88
		US A 5196143	23-03-93
		US A 5308547	03-05-94
		US A 5094778	10-03-92
DE A1 4122200	07-01-93	MX A1 9203932	02-03-93

WD A1 930126' 21-01-93

WD A1 9403574	17-02-94	keine - none - rien
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